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In Situ XAFS Characterization of the Nanostructural and Electronic Properties of Pt/C and PtNi/C as Cathode Catalysts in PEMFCs

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The electrocatalysis enhancement of Pt-based binary alloys (PtM), in comparison of pure Pt, has been systematically investigated by conducting *in situ* x-ray absorption spectroscopy characterization of PtNi/C and Pt/C nanoparticles as cathode catalysts in an Air-Breathe fuel cell. We observed that Pt-O formation at higher operation potentials was significantly inhibited in PtNi alloys, which prevents free active sites from being poisoned by oxygen adsorbate, leading to better reactivity. Two effects were confirmed to account for the inhibition. Electronic effect is the Ni reduces the bond strength of Pt-O by modifying the physical (geometric effect) and electronic (ligand effect) properties of Pt. Its side effect, an increase of open circuit voltage, was also detected. Attraction effect is that the more reactive alloying element (Ni) attracts and holds oxygen adsorbate more strongly than Pt. Furthermore, the reactivity trends among transition elements as alloyed metal in PtM was simulated by Feff calculation. Our development of the electrocatalysis enhancement mechanism can be a guidance to search for powerful catalysts in replacement of Pt.